

09/936980

31223-81174
(F-784)

TRANSMITTAL LETTER
TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US)
FOR ENTRY INTO THE U.S. NATIONAL PHASE (Chapter 2)

INTERNATIONAL APPLICATION NO. PCT/EP00/02573	INTERNATIONAL FILING DATE March 20, 2000	PRIORITY DATE CLAIMED March 19, 1999
TITLE OF THE INVENTION Polypropylene Having Improved Long Chain Branching		
APPLICANT(S) FOR DO/EO/US Yves Charlier		
PRIORITY APPLICATION NO. BE 99105661.5 (filed March 19, 1999)		

Via Express Mail

Box PCT
 Assistant Commissioner for Patents
 Washington, DC 20231

Dear Sir:

EXPRESS MAIL CERTIFICATE OF MAILING

Express Mail Mailing Label No. EL 465 446 455 US

I hereby certify that the papers enclosed herein are being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated below and addressed to: BOX PCT, Assistant Commissioner for Patents, Washington, DC 20231.

Clare Jackson
 Clare Jackson

September 19, 2001

Date of Deposit

Submitted herewith under cover of Form PTO-1390 is a copy of the International Application as filed (35 U.S.C. § 371(c)(2)). An English language translation of the application is not required since the International Application is being filed in English.

Submitted herewith is a check in the amount of \$1,260.00 as the fee for entry into the national phase as calculated on the attached Form PTC-1390. An oath or declaration of the inventor under 35 U.S.C. § 371(c)(4) will be submitted later.

Respectfully submitted,

William D. Jackson
 William D. Jackson
 Registration No. 20,846

Date: September 19, 2001

09/936980

JC03 Rec'd PGT/PTO 1 8 SEP 2001

Locke Liddell & Sapp LLP
2200 Ross Avenue, Suite 2200
Dallas, TX 75201
Telephone: 214/740-8000
Direct Dial: 214/740-8535
Facsimile: 214/740-8800

09/936980

1917 1918 1919 1920 1921 1922 1923 1924 1925 1926 1927 1928 1929 1930 1931 1932 1933 1934 1935 1936 1937 1938 1939 1940 1941 1942 1943 1944 1945 1946 1947 1948 1949 1950 1951 1952 1953 1954 1955 1956 1957 1958 1959 1960 1961 1962 1963 1964 1965 1966 1967 1968 1969 1970 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980 1981 1982 1983 1984 1985 1986 1987 1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023 2024 2025 2026 2027 2028 2029 2030 2031 2032 2033 2034 2035 2036 2037 2038 2039 2040 2041 2042 2043 2044 2045 2046 2047 2048 2049 2050 2051 2052 2053 2054 2055 2056 2057 2058 2059 2060 2061 2062 2063 2064 2065 2066 2067 2068 2069 2070 2071 2072 2073 2074 2075 2076 2077 2078 2079 2080 2081 2082 2083 2084 2085 2086 2087 2088 2089 2090 2091 2092 2093 2094 2095 2096 2097 2098 2099 2100 2101 2102 2103 2104 2105 2106 2107 2108 2109 2110 2111 2112 2113 2114 2115 2116 2117 2118 2119 2120 2121 2122 2123 2124 2125 2126 2127 2128 2129 2130 2131 2132 2133 2134 2135 2136 2137 2138 2139 2140 2141 2142 2143 2144 2145 2146 2147 2148 2149 2150 2151 2152 2153 2154 2155 2156 2157 2158 2159 2160 2161 2162 2163 2164 2165 2166 2167 2168 2169 2170 2171 2172 2173 2174 2175 2176 2177 2178 2179 2180 2181 2182 2183 2184 2185 2186 2187 2188 2189 2190 2191 2192 2193 2194 2195 2196 2197 2198 2199 2200 2201 2202 2203 2204 2205 2206 2207 2208 2209 2210 2211 2212 2213 2214 2215 2216 2217 2218 2219 2220 2221 2222 2223 2224 2225 2226 2227 2228 2229 2230 2231 2232 2233 2234 2235 2236 2237 2238 2239 2240 2241 2242 2243 2244 2245 2246 2247 2248 2249 2250 2251 2252 2253 2254 2255 2256 2257 2258 2259 2260 2261 2262 2263 2264 2265 2266 2267 2268 2269 2270 2271 2272 2273 2274 2275 2276 2277 2278 2279 2280 2281 2282 2283 2284 2285 2286 2287 2288 2289 2290 2291 2292 2293 2294 2295 2296 2297 2298 2299 2300 2301 2302 2303 2304 2305 2306 2307 2308 2309 2310 2311 2312 2313 2314 2315 2316 2317 2318 2319 2320 2321 2322 2323 2324 2325 2326 2327 2328 2329 2330 2331 2332 2333 2334 2335 2336 2337 2338 2339 2340 2341 2342 2343 2344 2345 2346 2347 2348 2349 2350 2351 2352 2353 2354 2355 2356 2357 2358 2359 2360 2361 2362 2363 2364 2365 2366 2367 2368 2369 2370 2371 2372 2373 2374 2375 2376 2377 2378 2379 2380 2381 2382 2383 2384 2385 2386 2387 2388 2389 2390 2391 2392 2393 2394 2395 2396 2397 2398 2399 2400 2401 2402 2403 2404 2405 2406 2407 2408 2409 2410 2411 2412 2413 2414 2415 2416 2417 2418 2419 2420 2421 2422 2423 2424 2425 2426 2427 2428 2429 2430 2431 2432 2433 2434 2435 2436 2437 2438 2439 2440 2441 2442 2443 2444 2445 2446 2447 2448 2449 2450 2451 2452 2453 2454 2455 2456 2457 2458 2459 2460 2461 2462 2463 2464 2465 2466 2467 2468 2469 2470 2471 2472 2473 2474 2475 2476 2477 2478 2479 2480 2481 2482 2483 2484 2485 2486 2487 2488 2489 2490 2491 2492 2493 2494 2495 2496 2497 2498 2499 2500 2501 2502 2503 2504 2505 2506 2507 2508 2509 2510 2511 2512 2513 2514 2515 2516 2517 2518 2519 2520 2521 2522 2523 2524 2525 2526 2527 2528 2529 2530 2531 2532 2533 2534 2535 2536 2537 2538 2539 2540 2541 2542 2543 2544 2545 2546 2547 2548 2549 2550 2551 2552 2553 2554 2555 2556 2557 2558 2559 2560 2561 2562 2563 2564 2565 2566 2567 2568 2569 2570 2571 2572 2573 2574 2575 2576 2577 2578 2579 2580 2581 2582 2583 2584 2585 2586 2587 2588 2589 2590 2591 2592 2593 2594 2595 2596 2597 2598 2599 2600 2601 2602 2603 2604 2605 2606 2607 2608 2609 2610 2611 2612 2613 2614 2615 2616 2617 2618 2619 2620 2621 2622 2623 2624 2625 2626 2627 2628 2629 2630 2631 2632 2633 2634 2635 2636 2637 2638 2639 2640 2641 2642 2643 2644 2645 2646 2647 2648 2649 2650 2651 2652 2653 2654 2655 2656 2657 2658 2659 2660 2661 2662 2663 2664 2665 2666 2667 2668 2669 2670 2671 2672 2673 2674 2675 2676 2677 2678 2679 2680 2681 2682 2683 2684 2685 2686 2687 2688 2689 2690 2691 2692 2693 2694 2695 2696 2697 2698 2699 2700 2701 2702 2703 2704 2705 2706 2707 2708 2709 2710 2711 2712 2713 2714 2715 2716 2717 2718 2719 2720 2721 2722 2723 2724 2725 2726 2727 2728 2729 2730 2731 2732 2733 2734 2

Polypropylene resin is used in a variety of different applications. However, polypropylene resin suffers from the problem of having a low melt strength, which restricts the use of polypropylene in a number of applications because the polypropylene is difficult to process. It is known in the art to increase the melt strength of polypropylene, for example by irradiating the polypropylene with an electron beam. It is known that electron beam irradiation significantly modifies the structure of a polypropylene molecule. The irradiation of polypropylene results in chain scission and grafting (or branching) which can occur simultaneously. Up to a certain level of irradiation dose, it is possible to produce from a linear polypropylene molecule having been produced using a Ziegler-Natta catalyst, a modified polymer molecule having free-end long branches, but the properties are not significantly improved.

For example, US-A-5554668 discloses a process for irradiating polypropylene to increase the melt strength thereof. An increase in the melt strength is achieved by decreasing the melt flow rate, otherwise known as the melt index. It is disclosed that

a linear propylene polymer material is irradiated with high energy ionising radiation, preferably an electron beam, at a dose rate in the range of from about 1 to 1×10^4 Mrads per minute for a period of time sufficient for a substantial amount of chain scission of the linear, propylene polymer molecule to occur but insufficient to cause gelation of the material. Thereafter, the material is maintained for a period of time sufficient but too long for a significant amount of long chain branches to form.

Finally, the material is treated to deactivate substantially all free radicals present in the irradiated material. In addition, the specification discloses the use of a very broad range of dose rates i.e. from 1 to 1×10^4 Mrads per minute. High dose rates of greater than about 40 Mrad can result in a substantially fully cross-linked structure of the polypropylene. Such a cross-linked structure is difficult to process.

CA-A-2198651 discloses a continuous method for producing polypropylene mixtures of increased stress-crack resistance and melt strength in which a low-energy electron beam accelerator with an energy of from 150 to 300 keV at a radiation dose of 0.05 to 12 Mrads is employed. This process also suffers from the disadvantage that the production rate of the irradiated powder can be somewhat low for commercial acceptance. Moreover, the polypropylene powder to be irradiated must be in the form of very fine particles. The specification discloses that bifunctional, unsaturated monomers can be added before and/or during the irradiation. Such compounds may include divinyl compounds, alkyl compounds, dienes, or mixtures thereof. These bifunctional, unsaturated monomers can be polymerised with the help of free radicals during the irradiation. However, no indication is given on how to proceed to improve the long chain branching of the polypropylene.

In order to prepare a cross-linked foam, a sheet of expandable resin composition is irradiated with ionising radiation to cross-link the resin. The ionising radiation may include electron rays, at a dose of from 1 to 20 Mrad. It is disclosed that auxiliary cross-linking agents may be employed which include a bifunctional monomer, exemplified by 1,9-nonanediol dimethacrylate.

US-A-2948666 and US-A-5605936 disclose processes for producing irradiated polypropylene. The latter specification discloses the production of a high molecular weight, non-linear propylene polymer material characterised by high melt strength by high energy irradiation of a high molecular weight linear propylene polymer. It is disclosed that the ionising radiation for use in the irradiation step may comprise electrons beamed from an electron generator having an accelerating potential of 500 to 4000 kV. For a propylene polymer material without a polymerised diene content, the dose of ionising radiation is from 0.5 to 7 Mrad. For propylene polymer material having a polymerised diene content, the dose is from 0.2 to 2 Mrad. But once again, there is no indication on the long chain branching.

EP-A-0821018 discloses the preparation of cross linkable olefinic polymers which have been subjected to ionising radiation. The specification exemplifies electron beams of relatively low energy and low doses to split polymeric chains in order to graft silane derivatives onto the polymeric chain. The specification does not address the problem of achieving high melt strength of polymers.

EP-A-0519341 discloses the grafting of vinyl monomers on particulate olefin polymers by irradiating the polymer and

treating thereafter with a grafting monomer. In an example, polypropylene is irradiated with an electron beam having an energy of 2 MeV and subsequently treated with maleic anhydride as a grafting monomer.

US-A-5411994 discloses the production of graft copolymers of polyolefins in which a mass of olefin polymer particles is irradiated and thereafter the mass is treated with a vinyl monomer in liquid form. The ionising radiation dose is about 1 to 12 Mrad and the ionising radiation preferably comprises electrons beamed from an electron generator having an accelerating potential of 500 to 4000 kV. The polymer is first irradiated and then treated with a grafting agent.

EP-A-0792905 discloses the continuous production of polypropylene mixtures of increased stress crack resistance and melt strength by the action of ionising radiation. The energy of the ionising radiation is from 150 to 300 keV and the radiation dose ranges from 0.05 to 12 Mrad.

The present invention aims to provide polypropylene resins having improved long chain branching as well as improved melt strength. More particularly the branching index of polypropylene of the invention should be lower than 0.7. It is also a goal of the invention to provide a process to prepare polypropylene with substantially increased long chain branching on the polypropylene molecules following the irradiation, while employing relatively low irradiation doses. It is a further aim to produce polypropylene having not only improved long chain branching and improved melt strength, but also improved recovery compliance and relaxation time.

Accordingly, the present invention provides for polypropylene having increased long chain branching particularly having a branching index of lower than 0.7 melt strength. It has been unexpectedly found that such improved long chain branching (LCB) polypropylene may be obtained by irradiating polypropylene with an electron beam having an energy of at least 5 MeV and with a radiation dose of from 5 to 100 kGray in the presence of a grafting agent for forming long chain branches on the polypropylene molecules.

It has also been unexpectedly found that such improved LCB polypropylene may be obtained with high energies owing to the conjoint use of a grafting agent during the irradiation step.

Such improvement has been found and finally measured through the determination of the branching index.

The branching index as mentioned in the present patent application is obtained by the ratio of weight average MW values inferred from rheological measurement at zero shear viscosity and at crossover points as fully described in Polymer Testing 11, 89 (1992) by K. Bernreitner et al.

Preferably, the polypropylene is irradiated at an energy of at least 10 MeV.

The polypropylene may be a homopolymer of propylene or a random or block copolymer of propylene and one or more olefins and/or dienes selected from ethylene and C₄ to C₁₀ 1-olefins or dienes, which may be linear or branched. The polypropylene homopolymer may be reinforced by rubber particles, for example ethylene-propylene rubber particles, typically in an amount of up to 30wt%. The polypropylene may be a terpolymer optionally with a

diene, for example norbornadiene, as a comonomer.

According to the present invention, the polypropylene to be irradiated is mixed prior to irradiation with the grafting agent which increases the long chain branching of the propylene molecules as a result of the irradiation. The grafting agent is directly incorporated into the propylene molecule during the irradiation step. The grafting agent includes at least one carbon-carbon double bond, and preferably is polyunsaturated, being for example bi, ter or tetra unsaturated. The non-conjugated unsaturated compounds are preferred, although conjugated saturated compounds may be employed. The grafting agent may contain polar groups, such as ester, anhydride, or imide groups and/or non-metallic elements such as silicon, phosphorous and halogen atoms. The grafting agent may be selected from the group consisting of bismaleimide derivatives; mono-, di-, tri-, tetra-acrylate or methacrylate compounds; organosilane compounds of the formula $A_{4-n}SiR_n$ where A are identical or different acrylate or methacrylate or vinyl groups, where R are identical or different alkoxy or acetoxy groups and where n is 1, 2, 3 or 4; α,β -unsaturated acids and their anhydride derivatives; non-conjugated dienes such as 1,5-hexadiene, norbornadiene and dicyclopentadiene; dipentene; polybutadiene and copolymers containing polybutadiene blocks; butadiene based polymers and copolymers; polyisoprene and copolymers containing polyisoprene blocks; isoprene based polymers and copolymers; polyethylene; C_{4-20} α -olefins either linear or branched; styrene or divinylbenzene; ethylene-propylene rubbers and ethylene-propylene-diene rubbers; di-furnane derivatives; ester derivatives of fatty acids; and vinylpolybutadiene.

A particularly preferred grafting agent comprises tetravinyl

silane.

The grafting agent employed in accordance with a preferred aspect of the invention results, following irradiation, in polypropylene molecules having some free end terminations, with a cross-link density which is not so high as to reduce the processability of the polymer.

In a further preferred aspect, functional monomers such as maleic anhydride, styrene, acrylic acid, methacrylic acid, 1,4-butanediol diacrylate, or ethylene glycol dimethacrylate may be incorporated into the polypropylene resin. These functional comonomers promote long chain branching of the polypropylene molecules.

In a particularly preferred embodiment of the invention, polypropylene homopolymer in fluff or powder form in an oxygen-free environment is mixed with a grafting agent. Preferably, the grafting agent comprises from 0.01 to 5 wt% of the weight of the polypropylene, more preferably from 0.01 to 1 wt% of the weight of the polypropylene. A particularly preferred grafting agent comprises tetravinyl silane in an amount of from 0.01 to 1wt% based on the weight of the polypropylene, most particularly from 0.01 to 0.5 wt% based on the weight of the polypropylene.

The polypropylene/grafting agent mixture is thereafter deposited onto a continuously moving conveyor such as an endless belt. The mixture on the conveyor passes under an electron beam generator which irradiates the mixture. The accelerating potential or energy of the electron beam is at least 5 MeV, more preferably from 5 to 100 MeV, still more preferably at least 10 MeV, yet more preferably from 10 to 25 MeV. The power of the electron beam generator is preferably from 50 to 500 kW more preferably

for 120 to 250 kW. The radiation dose to which the polypropylene/ grafting agent mixture is subjected is preferably from 10 to 100 kGray, preferably around 15 kGray (10 kGray is equivalent to 1 Mrad). The conveyor speed is adjusted in order to achieve the desired dose. Typically, the conveyor speed is from 0.5 to 20 metres/minute, preferably from 1 to 10 metres/minute, more preferably from 2.25 to 8.5 metres/minute.

As a result of the high irradiating potential of the electron beam, not only can the conveyor speed be significantly higher than in the prior art, but also the thickness of the continuously moving bed of polypropylene/grafting agent mixture on the conveyor can be relatively high. Typically, the bed of polypropylene homopolymer and grafting agent has a thickness of up to 20 cm, most particularly from 5 to 10 cm. The bed of polypropylene homopolymer/grafting agent mixture on the conveyor typically has a width of up to about 1 metre. The irradiation is carried out under an inert atmosphere, such as nitrogen.

After irradiation by the electron beam, the polypropylene powder can be annealed and then treated with at least one known antioxidant additive. The annealing temperature may range from 50 to 150°, more preferably from 80 to 120°C and the annealing time may range from 1 to 60 minutes, more preferably from 5 to 30 minutes. Thereafter the polypropylene is granulated.

In accordance with the invention, the irradiated polypropylene has increased recovery compliance, relaxation time and melt strength. These particular rheological properties provide an outstanding processing behaviour which allows the polypropylene based polymers produced in accordance with the invention to be suitable particularly for producing films, sheets, fibres, pipes, foams, hollow articles, panels and coatings. The irradiated

polypropylene also has improved mechanical properties, such as flexural modulus and impact resistance.

The invention will now be described in greater detail with reference to the following non-limiting example and the accompanying drawing, in which:-

Figure 1 is a graph showing the relationship between melt strength and temperature for high melt strength polypropylene produced in accordance with an embodiment of the process of the invention and two other polypropylenes not produced in accordance with the invention.

EXAMPLE

In accordance with the example, a polypropylene homopolymer fluff in the form of a powder having a median particle size (d_{50}) of from 1000 to 1500 microns, a bulk density of around 0.5g/cc and having a melt flow index (MFI) of 1.0 g/10min was treated by irradiation. In this specification the melt flow index (MFI) is measured by the procedure of ASTM D 1238 using a load of 2.16kg at a temperature of 230°C. The polypropylene powder had been treated under pure nitrogen since the presence of oxygen is detrimental to the irradiation process.

The polypropylene powder was then mixed with a grafting agent comprising tetravinyl silane in an amount of 0.5wt% based on the weight of the polypropylene powder. Thereafter, the mixture of the polypropylene powder and the grafting agent was subjected to electron beam irradiation.

In particular, the polypropylene powder and grafting agent mixture was deposited onto an endless belt conveyor having a speed of 8.5 metres per minute. The polypropylene

powder/grafting agent mixture was deposited onto the conveyor as a 1 metre wide bed having a thickness of 7 cm. The conveyor conveyed the bed underneath a high energy high power electron accelerator. Such accelerators are available in commerce. The accelerator had an energy of 10 MeV and a power of 120 kW. The polypropylene powder/grafting agent mixture was irradiated for a period of time (determined by the conveyor speed) sufficient to provide a radiation dose of 15 kGray. During the irradiation, the powder was maintained under nitrogen to exclude oxygen.

After irradiation, the powder was mixed with conventional antioxidant additives. Thereafter, the powder was granulated under nitrogen gas.

In order to demonstrate the benefits of the present invention, a number of samples were tested to determine their properties, with one of the samples being processed in accordance with the method of the present invention, and the remaining samples not being processed in accordance with the method of the present invention. Thus referring to Table 1, seven samples, with their respective treatments, are indicated.

Sample 3 corresponds to the above-described Example in which the specified polypropylene resin was irradiated by the electron beam at the dose and conveyor speed specified in Table 1, with the polypropylene having being mixed with tetravinyl silane grafting agent prior to irradiation.

The remaining samples 1, 2 and 4 to 7 are not in accordance with the invention but are included so as to show comparatively the benefits of the invention exemplified by sample 3.

Sample 1 corresponds to the same polypropylene as employed for

sample 3, but which was not irradiated; in other words it was the original polypropylene material.

Sample 2 corresponds to the same polypropylene material which was subjected to irradiation under the dose and conveyor speed specified in Table 1, with the polypropylene not having been mixed with a grafting agent prior to irradiation.

Sample 4 corresponds to the same polypropylene which was subjected to the same irradiation treatment as sample 2, but then the polypropylene was annealed after the irradiation step to facilitate recombination of any remaining radicals. The annealing temperature was 120° and the annealing time was 30 minutes.

For each of samples 2 and 4, it may be seen that the dose of irradiation is significantly higher than that for sample 3 in accordance with the invention, and that the conveyor speed is significant lower than that for sample 3 of the invention. This is because in the absence of a grafting agent, in order to achieve a reasonable level of branching following irradiation, not only must the dose be very high but also the conveyor speed must be considerably lower in order to increase the irradiation time to ensure that a reasonable level of branching is achieved. This significantly reduces the production rate of the irradiated polypropylene. The higher dose required for samples 2 and 4 increases the production costs.

In Table 1, samples 5, 6 and 7 correspond to three respective commercially available polypropylene resins with melt flow index of around 3g/10 min. Profax PF 184 is available in commerce from the company Montell North America, Inc. of Wilmington, Delaware, United States of America and comprises a polypropylene

homopolymer which has been irradiated by a low density electron beam at a high irradiation dose. The product Daploy 130 D is a polypropylene resin available in commerce from the company PCD Polymere GmbH of Schwechat-Mannsworth, Austria. The product FINAPRO PPH 4060 is a polypropylene resin available in commerce from the company Fina Chemicals of Belgium. Samples 5 and 6 are high melt strength polypropylene resins with long chain branching and sample 7 is a linear polypropylene homopolymer.

The branching index has been measured for all the samples and it can be seen from Table 1 the significant improvement in the long chain branching of the polypropylene of the invention.

By way of information, a linear polymer has a branching index of about 1 while a branched polymer presents a branching index lower than 1.

Referring to Table 2, the melt flow index (MFI) of each of the seven samples was measured. It will be seen that sample 3, corresponding to the polypropylene produced in accordance with the method of the present invention, had the lowest melt flow index of 0.86 g/10min. This demonstrates that the use of grafting agent promotes the recombination of macroradicals and reduces the incidence of chain scission when compared to samples 2 and 4.

The MFI of sample 1 was increased by irradiation to form sample 2 as a result of chain scission caused by the radiation.

When a grafting agent is not used, there is no improvement at all for the long chain branching.

For samples 1 to 6 the mechanical properties of extrusion force at 250°C, melt strength at 250°C, 270°C and 290°C and speed at

break 250°C, 270°C and 290°C were measured and the results are shown in Table 3. The melt strength is the force, measured in milliNewtons (mN) that is required to draw a polymer in the molten state. In this specification, the melt strength has been measured using a rheological device for capillary and tensile rheometry on polymer melts, such as a CEAST 1000 rheometer. In this specification, the polymer is melted and extruded through a capillary die. The extrusion force, or the force which is applied to the melt to be extruded through the capillary die at a constant flow rate, is measured in newtons (N). The filament is drawn by stretching or elongation as a result of being attached to a roll which is rotating with a constant acceleration of 10 rpm per 100 seconds, with an initial rotational speed of 2 rpm. The force required to draw the filament is recorded continuously and is expressed in milliNewtons (mN). The force increases with an increase in the rotational speed of the roll until the force reaches a plateau, which is recorded as the final value of the melt strength. It is this final value which is specified in Table 3. Additionally, the rotational speed at which the filament breaks is also determined and is expressed as an instantaneous rotational speed in rpm and corresponds to the speed at break specified in Table 3. It may be seen that for sample 3 produced in accordance with the invention, this shows a high level of melt strength, particularly over a range of processing temperatures and rather a low speed at break. Samples 5 and 6 lose their melt strength at 290°C and are spinnable as a standard product. At 290°C sample 3 has a good level of melt strength. In contrast, samples 2 and 4 show a limited increase of melt strength.

Figure 1 shows for samples 3, 5 and 6 the relationship between melt strength and temperature. It may be seen that for sample

3, as compared to samples 5 and 6, the rate of decrease of melt strength of temperature is significantly reduced. Moreover, it may also be seen that the polypropylene of sample 3 still has a high melt strength at 290°C, while the polypropylenes of samples 5 and 6 have no significant melt strength at that temperature.

Thus the process of the present invention enables the production of high melt strength polypropylenes which have good melt strength at high temperatures, enabling them to be processed, for example to produce spun fibres, at high processing temperatures.

It may be thus seen in accordance with the invention that the use of the process of the invention can provide a polypropylene having a high melt strength which is a strong advantage when the molten polymer is being processed, for example when being blown into film, extruded into pipes, spun into fibres, or formed as a foam.

Referring to Table 4, this shows the values of the flexural modulus and the impact resistance for sample 3 produced in accordance with the invention, and for samples 1, 5, 6 and 7.

The flexural modulus was measured using the procedure of ISO 178 and the impact resistance was measured using the IZOD test at 23°C of the procedure of ISO R180/1A. Comparing the polypropylene of sample 3 with that of sample 1, it may be seen that the use of high energy electron beam irradiation in combination with the grafting agent for forming long chain branches on the polypropylene molecules increases both the flexural modulus and the impact resistance of the polypropylene, while keeping substantially the same melt flow index. The mechanical properties of the polypropylene are improved, while maintaining substantially the same melt flow properties of the polypropylene. Comparing the polypropylene of sample 3 produced in accordance with the invention with those of samples 5, 6 and

7 which are commercially available polypropylenes, it may be seen that the flexural modulus of the polypropylene produced in accordance with the invention is either the same as or significantly greater than the flexural modulus of those known commercial polypropylenes, and also compared to all three samples 5, 6 and 7 sample 3 has a significantly higher impact resistance, for example at least about 50% higher than for the known polypropylene. Thus the process of the present invention enables a polypropylene having improved mechanical properties, as well as increased melt strength, to be achieved.

The recovery compliance and relaxation time were measured for samples 1 to 7 and the results are shown in Table 5. In accordance with the invention the recovery compliance and relaxation times of sample 3 are higher than that for samples 2 and 4 where no grafting agent was employed. Moreover, for sample 3 produced in accordance with the invention, the relaxation time was significantly higher than that for all the other samples.

These results clearly show the advantage of adding a grafting agent prior to the irradiation step.

TABLE 1

Sample	Treatment	Dose (kGray)	Conveyor Speed (m/min)	Branching Index
1	Non-irradiated PP	-	-	-
2	Irradiated PP	60	2.1	0.89
3	Irradiated PP in the presence of a grafting agent	15	8.5	0.52
4	Irradiated PP and annealed	60	2.1	0.83
5	Profax PF 814	Not Known	Not Known	0.72
6	Daploy 130 D	Not Known	Not Known	0.7
7	FINAPRO PPH 4060 non-irradiated	-	-	1.01

TABLE 2

Sample	MFI (g/10')
1	1.0
2	3.0
3	0.86
4	4.0
5	3.1
6	2.98
7	3.0

TABLE 3

Sample	Extrusion force (daN)	Melt strength (mN)			Speed at break (rpm)		
		250°C	270°C	290°C	250°C	270°C	290°C
1	8	8	-	-	>240	-	-
2	3	17	-	-	35	-	-
3	8	45	35	15	3	3	3
4	3	17.5	-	-	35	-	-
5	3	50	20	1.5	9	25	170
6	-	-	40	2	-	5	-

TABLE 4

Sample	Flexural modulus (MPa)	Impact resistance (kJ/m ²)
1	1615	4.5
3	1955	7.3
5	1685	3.2
6	2020	5.5
7	1360	4.8

TABLE 5

Sample	Recovery Compliance (1x10 ⁻⁴ /Pa)	Relaxation Time (sec)
1	3.1	6.5
2	12.0	10.6
3	29.4	106.0
4	11.7	10.9
5	35.2	15.0
6	49.8	28.3
7	5.5	2.9

CLAIMS:

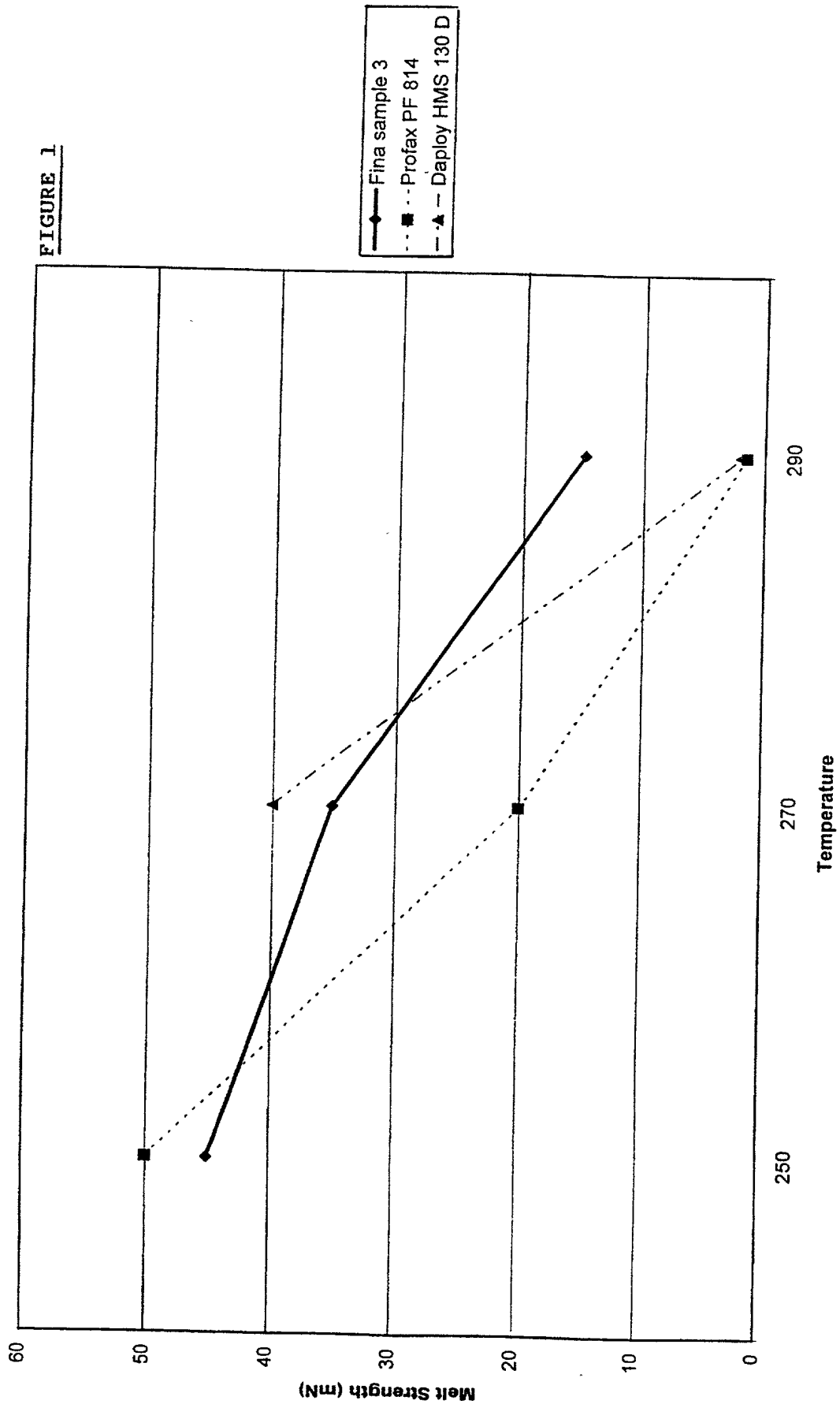
1. Polypropylene having improved long chain branching and increased melt strength characterized in that it is produced by irradiating polypropylene with an electron beam having an energy of at least 5 MeV with a radiation dose of from 5 to 100 kGray in the presence of a grafting agent.

2. A polypropylene according to claim 1 wherein the electron beam energy to be used is of at least 10 MeV.

3. A polypropylene according to claim 1 or 2 wherein the grafting agent is selected from the group consisting of bismaleimide derivatives; mono-, di-, tri-, tetra-acrylate or methacrylate compounds; organosilane compounds of the formula A_nSiR_n where A are identical or different acrylate or methacrylate or vinyl groups, where R are identical or different alkoxy or acetoxy groups and where n is 1, 2, 3 or 4; α,β -unsaturated acids and their anhydride derivatives; non-conjugated dienes such as 1,5-hexadiene, norbornadiene and dicyclopentadiene; dipentene; polybutadiene and copolymers containing polybutadiene blocks; butadiene based polymers and copolymers; polyisoprene and copolymers containing polyisoprene blocks; isoprene based polymers and copolymers; polyethylene; C_{4-20} α -olefins either linear or branched; styrene or divinylbenzene; ethylene-propylene rubbers and ethylene-propylene-diene rubbers; di-furnane derivatives; ester derivatives of fatty acids; and vinylpolybutadiene.

4. A polypropylene according to any one of claims 1 to 3 wherein the grafting agent comprises from 0.01 to 5 wt% of the weight of the polypropylene.

5. A polypropylene according to any one of claims 1 to 4 wherein the grafting agent comprises tetravinyl silane.
6. A polypropylene according to claim 5 wherein the tetravinyl silane is in an amount of from 0.01 to 1 wt% based on the weight of the polypropylene.
7. Polypropylene having a branching index of lower than 0.7 and an improved melt strength obtained by irradiating a polypropylene with an electron beam energy of at least 5 MeV with a radiation dose of 5 to 100 kGray in the presence of a grafting agent.
8. A process to produce a polypropylene with improved long chain branching and high melt strength in accordance with anyone of the preceding claims.

FIGURE 1

DECLARATION

As below named inventor, I, YVES CHARLIER, hereby declare that:

My residence address and citizenship are as stated below next to my name;

I believe I am the original, first and sole inventor of the subject matter which is described and claimed and for which a patent is sought on the invention, design or discovery entitled: POLYPROPYLENE HAVING IMPROVED LONG CHAIN BRANCHING, the specification of which was filed on March 20, 2000, as International Application No. PCT/EPO 00/02573, and on September 19, 2001, as U.S. Application Serial No. 09/936,980.

I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above;

I do not know and do not believe that said invention, design or discovery was ever known or used in the United States of America before our invention or discovery thereof, or patented or described in any printed publication in any country before our invention or discovery thereof, or more than one year prior to this application, or in public use or on sale in the United States of America more than one year prior to this application; that said invention, design or discovery has not been patented or made the subject of an inventor's certificate issued prior to the date of this application in any country foreign to the United States of America on an application filed by my legal representatives or assigns; and that I acknowledge my duty to disclose information of which I am aware which is material to patentability in accordance with 37 C.F.R. Section 1.56(a).

I hereby claim foreign priority benefits under 35 U.S.C. Section 119 of the foreign application(s) for patent or inventor's certificate listed below and have also identified below the foreign application for patent or inventor's certificate having a filing date before that of the application for which priority is claimed:

Number	Country	Date Filed
991056661.5	BE	March 19, 1999

Please send correspondence to:
to:

David J. Alexander
Fina Technology, Inc.
P.O. Box 674412
Houston, TX 77267-4412

Please direct telephone calls

David J. Alexander
(281) 227-5379

POWER OF ATTORNEY

We, ATOFINA Research, a corporation of the country of Belgium and having its principal offices at Zone Industrielle C, 7181 Seneffe (Feluy), Belgium, ASSIGNEE of the entire interest in the invention, application and any Letters Patent that may issue thereon for POLYETHYLENE FIBRES, the specification of which was filed on Sept. 19, 2001, as Application Serial No. 09/936,980, hereby appoint:

8
David J. Alexander, Registration No. 33,221
WILLIAM D. JACKSON, Registration No. 20,846;
L. DAN TUCKER, Registration No. 22,670;
ROY W. HARDIN, Registration No. 28,304;
MARTIN KORN, Registration No. 28,317;
MONTY L. ROSS, Registration No. 28,899;
CHARLES PHIPPS, Registration No. 40,127; and
MICHAEL DUBNER, Registration No. 47,310.

as our attorney with full power of substitution and revocation, to prosecute this application and to transact all business in the United States Patent and Trademark Office connected therewith, and to file and prosecute any international or foreign patent applications filed thereon before any international or foreign authorities.

Please send correspondence and direct phone calls to:

David J. Alexander
Fina Technology, Inc.
P.O. Box 674412
Houston, Texas 77267-4412
(281) 227-5379
Attorney Docket No. F-784

We declare that the below-named individual is authorized to execute this Power of Attorney on behalf of ASSIGNEE.

ASSIGNEE CERTIFICATION

In accordance with 37 CFR §3.73 the ASSIGNEE hereby certifies that the evidentiary documents with respect to its ownership have been reviewed and that, to the best of ASSIGNEE's knowledge and belief, title is in the ASSIGNEE seeking to take this action.

ATOFINA RESEARCH

Signature: _____

Name: J. C. DewartTitle: Department ManagerDate: 12 October 2001

de BRUYN Johan
Patent Formalities Officer

J.C. DEWART
Department
Manager

Serial No. 09/936,980
Attorney Docket No. F-784

Declaration - Yves Charlier
Page 2 of 2

I hereby declare that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

10) Full name of first inventor

Yves PAUL Charlier
First Middle Last

First inventor's signature



Residence: Chaussee de Braine-le-Comte, 79, B-1400 Nivelles, Belgium

BEX

Date 10/24/01
Citizenship: Belgium

2010-09-24 10:00:00